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Benzothiadiazole derivatives functionalized with two different (hetero) aromatic donor groups: Synthesis and evaluation as TiO_2 sensitizers for DSSCs

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ABSTRACT

A series of benzothiadiazole-based push-pull heterocyclic systems were synthesized and characterized in order to study the variations induced by different aromatic and heterocyclic donor groups in the optical, electronic and photovoltaic properties of DSSCs prepared with the respective cyanoacetic acid derivatives. The organic sensitizers bear a 5-hexyl-2,2′-bithienyl or *N,N*-diphenylanilino donor moieties conjugated with a thienyl-benzothiadiazole spacer functionalized with the electron acceptor/anchoring cyanoacetic acid group. The solar cell based on TiO_2 sensitized with the novel dye bearing the 5-hexyl-2,2′-bithienyl donor, exhibited a power conversion efficiency of 0.95 % due the inefficient electron injection. Co-adsorption studies of the same dye resulted in enhanced photovoltaic conversion efficiency of 2.49 %, which represents an improvement of cell efficiency of 260 %. The sensitizer bearing the *N,N*-diphenylanilino donor exhibited 4.51 % power conversion efficiency, that was further enhanced by co-sensitization to 5.22 % efficiency.

1. Introduction

Among the diverse renewable energy sources available, solar energy is a very interesting option due to its inexhaustibility, cleanness, and the capacity to be converted directly into electrical power by photovoltaic cells devices [1]. Consequently, solar cells based on organic dye sensitizers adsorbed on nanocrystalline TiO_2 have been the subject of vast studies mainly because of their good performance, simple architecture and low manufacturing cost. The dye sensitizer is a very important element since it affects the conversion efficiency as well as on the stability of the cells [2]. For the last several years, push-pull π-conjugated systems (D-π-A) have been recognized as excellent candidates for high-performance organic dyes as this particular molecular arrangement allows the interaction of the electron donor and acceptor end-caps, through a π-conjugated spacer that favors a new low energy molecular orbital with visible light excitation (colored compounds), and is responsible for the polarization of the chromophore and generation of a molecular dipole [3]. π-Conjugated heterocyclic systems are usually easy to synthesize and exhibit excellent optical and electrochemical properties. Moreover, their structures can easily be tuned in order to modulate their optical and electrochemical properties, and thermal stability. Therefore, in the last two decades several studies concerning the structure to properties relation have been performed having in mind practical applications such as field-effect transistors (OFETs) [4], light emitting diodes (OLEDs) [5], nonlinear optics (SHG, TPA) [6], photovoltaic cells (OPVCs) [7], dye-sensitized solar cells (DSSCs) [8], bulk heterojunction cells (BHJs) [9], near infrared absorbing (NIR) dyes [10], etc.

The tuning of the molecular properties of these systems for the desired applications can be achieved through modification of the electron donor or electron acceptor groups, modification of the π-bridge (conjugation length, electronic nature and polarizability), and varying the overall chromophore arrangement (planarity, and further auxiliary functionalization). It is well known that the incorporation of heterocycles with different electronic nature (electron-rich or electron deficient) into the π-conjugated systems will induces higher photochemical and thermal stabilities and will modulate its optoelectronic properties. Moreover, the position of the heterocycles on the π-bridges has also to be contemplated. In fact, due to their electronic nature and low aromaticity, they can act powerfully as π-bridges as well as auxiliary donors (electron-rich heterocycles: thiophene, pyrrole, furan) or as auxiliary acceptors (electron-deficient heterocycles: benzothiadiazole, pyridine, etc.) [3b,11].

Benzothiadiazole is a well-known electron deficient heterocycle that

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have been incorporated into a D-π-A′-π-A structures, improving their light harvesting and the photochemical stability. The auxiliary electron acceptor ability exhibit by this heterocycle is beneficial for modulating the energy levels and extending absorption wavelength. However, strong electron withdrawing ability can be treated as an "electron trap" which suppresses intramolecular charge transfer (ICT). Consequently, discovering a balance between the two aspects is a matter of significance. Several benzodiathiazole derivatives have been already reported as efficient dyes for DSSCs due to their higher photovoltaic efficiencies and remarkably enhanced ICT [2d,11a,12]. On the other hand, thiophene heterocycle acts simultaneously as an efficient electron-donor group and π-spacer [11b,11c,11d,13-14].

Having in mind previous studies [2d,3b,11a,12-13], as well as our experience on the modulation of redox, and optical properties of π-conjugated systems using the heterocyclic auxiliary electron donor or acceptor effect for optical and photovoltaic applications [2d,11b-d,13-14] we decided to expand our studies to the synthesis and evaluation of optical and redox properties of two benzothiadiazole-based push-pull heterocyclic systems as well as their application as sensitizers for DSSCs. The compounds are constituted by an electron-deficient benzothiadiazole moiety linked to a thiophene heterocycle functionalized with cyanoacetic acid that is a stable anchoring group with easy synthesis and better properties of DSSCs, due to its coplanarity with respect to spacer unit and good electron coupling with TiO_2 [15]. We designed a novel dye functionalized with the heterocyclic 5-hexyl-2,2′-bithienyl donor moiety due to its excellent charge transport properties and the sterically hindered *n*-hexyl chain is expected to suppress the aggregation tendency [14d,16]. A sensitizer bearing a *N*,*N*-dimethylanilino donor group/π-spacer was also prepared in order to study the effect of a different donor group in the optical and electrochemical properties of the dye, and in the photovoltaic properties of the DSSC prepared with TiO_2 sensitized with this dye.

2. Results and discussion

2.1. Synthesis and characterization of the push-pull systems 2–4

Two push-pull heterocyclic chromophores were prepared in order to study the effect of 5′-hexyl-2,2′-bithienyl donor moiety on the photophysical and redox properties, as well as the photovoltaic parameters of the dye when applied as sensitizer in DSSCs, when compared to the *N*,*N*-diphenylanilino donor group. All the compounds are constituted by a thienyl-benzothiadiazole spacer which is well-known to induce bathochromic shifts and improved light harvesting and photochemical stability.

Precursor **2** was prepared by Suzuki-Miyaura cross-coupling between the 4,7-dibromobenzo[*c*]-1,2,5-thiadiazole and 5-formyl-2-thiopheneboronic acid in moderate yield (40 %). Aldehyde precursors **3a-b** were prepared by Suzuki-Miyaura cross-coupling between precursor **2** and 4-(diphenylamino)phenylboronic acid pinacol ester or 5′-hexyl-2,2′-bithiophene-5-boronic acid pinacol ester, in good yields (56–61 %). The final push-pull dyes **4a-b** were synthesized in moderate yields (43–51 %) by Knoevenagel condensation of the corresponding aldehyde precursors **3** with 2-cyanoacetic acid in refluxing acetonitrile, using piperidine as catalyst (Scheme 1).

We are aware that the synthesis and evaluation of dye **4b** as TiO_2 sensitizer in DSSC have already been reported [17]. Nevertheless, we decide to prepare this compound in order to perform the comparative study of this benzodithiazole derivative with dye **4b** bearing a 5′-hexyl-2,2′-bithienyl heterocyclic donor group.

The structures of the heterocyclic compounds were confirmed by standard analytical and spectroscopic techniques (detailed analysis are presented in SI, Table S1).

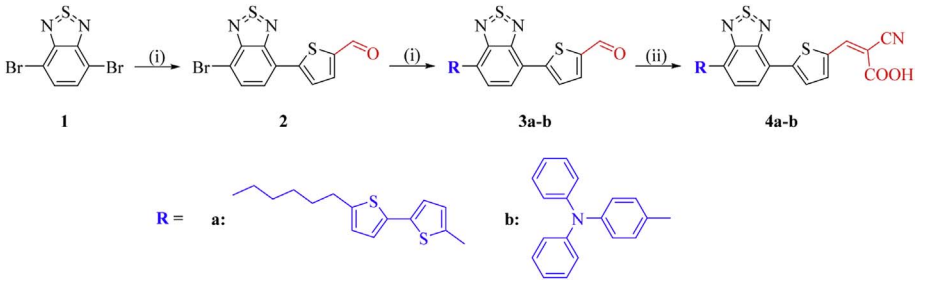
2.2. Study of the optical properties of push-pull systems 3–4

The optical properties of heterocyclic compounds **3–4** were investigated in ethanol at 21 ± 2 °C, and the experimental data are presented in Table 1. The UV–vis spectra of compounds **2–3** are shown in Fig. 1. All push-pull chromophores **3–4** exhibit a strong and broad band between 475 and 506 nm due to π→π* transitions, that can be assigned to an internal charge transfer between the electron donor and acceptor groups. A second absorption band is also noticeable for all chromophores at shorter wavelengths (<375 nm). A bathochromic shift of the absorption maxima was also observed by substituting the *N*,*N*-diphenylanilino for the 5′-hexyl-2,2′-bithienyl moiety, that can be attributed to the lower electron donating ability of *N*,*N*-diphenylanilino group due to the partial delocalization of the nitrogen nonbonding lone pair to the conjugated phenyl units that are usually organized in a nonplanar fashion, and to the bathochromic effect of sulphur [3b,14d-e]. The bathochromic shifts of dyes **4a-b** can be ascribed to the longer π-conjugation and stronger electron withdrawing strength of the cyanoacetic group, when compared to the respective formyl precursors **3a-b**. The synthesized dyes **3–4** exhibit high molar extinction coefficients in the range of 23,769–31,460 M^{-1} cm^{-1}.

Compounds **3–4** were excited at the wavelength of maximum absorption, at room temperature, in order to study their fluorescence properties (Table 1, Fig. 1). The nature of the donor group significantly effects on the fluorescence. The emission spectra of compounds **3a-b** and **4a-b** followed the same trend described above for the absorbance. Benzothiadiazoles **3a-b** and **4a-b**, show emissions at 644, 657, 625, and 655 nm, respectively. A red shift of the λ_{em} of the compounds **3–4** is observed and is attributed to stronger electron donating or electron withdrawing abilities of the donor and acceptor groups, respectively, and to an increase in the π-conjugation path length. Compounds **3a** and **4a**, bearing the 5′-hexyl-2,2′-bithienyl donor moiety show good to moderate emissive properties (ϕ_F = 0.59 for **3a**, ϕ_F = 0.21 for **4a**), while compounds **3b** and **4b** bearing a triphenylamine donor group exhibit moderate to weak emissive properties (ϕ_F = 0.15 for **3b**, ϕ_F = 0.08 for **4b**). The lower relative fluorescence quantum yields observed for the *N*,*N*-diphenylaniline derivatives **3b** and **4b** is due to the distortion of this group, leading to loss of conjugation [18].

2.3. Study of the electrochemical properties of dyes 4a-b by cyclic voltammetry

Cyclic voltammetry was used to study the redox behavior of compounds **4a-b**, and to obtain the HOMO and LUMO energy levels of the



Scheme 1. Synthesis of precursor **2** and push-pull heterocyclic dyes **3a-b** and **4a-b**: (i); DME, $Pd(PPh_3)_4$, N_2, EtOH, R-$B(OH)_2$, Na_2CO_3 (ii) 2-cyanoacetic acid, acetonitrile, piperidine, reflux.

molecules. The HOMO and LUMO energies of compounds **4** were calculated with respect to ferrocene reference (4.39 eV). The data is summarized in Table 2.

Compounds **4a-b** exhibit very different oxidation potentials, which is in agreement with the different electronic nature of the aromatic (*N*,*N*-diphenylanilino) or heterocyclic (5′-hexyl-2,2′-bithienyl) nature of the donor group. Compounds **4** show reversible redox behavior as potentials of anodic and cathodic current peaks of their oxidation and reduction remain constant whatever scan rate of potential is applied. Compound **4b** exhibits oxidation potential (0.72 V) higher than that of the $3I^-/I_3^-$ couple (0.42 V). However, dye **4a** shows low oxidation potential (0.35 V), resulting in an ineffective regeneration of the dye by the electrolyte. Dyes **4a-b** show similar energy of LUMO, nonetheless, dye **4a** presents higher LUMO energy (−2.59 eV for **4a** and, −2.61 for **4b**), suggesting a slightly stronger thermodynamic driving force for electron injection into conduction band of TiO_2. Additionally, dye **4a** has the lowest band gap (2.15 eV) of the synthesized dyes.

Table 1
Absorption and emission data for push-pull heterocyclic dyes **3–4** in ethanol.

Cpds	Absorption		Emission		
	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	ϕ_F	Stokes' shift (nm)
3a	495	31,640	644	0.59	149
3b	475	26,393	657	0.15	182
4a	506	28,556	625	0.21	119
4b	482	23,769	655	0.08	173

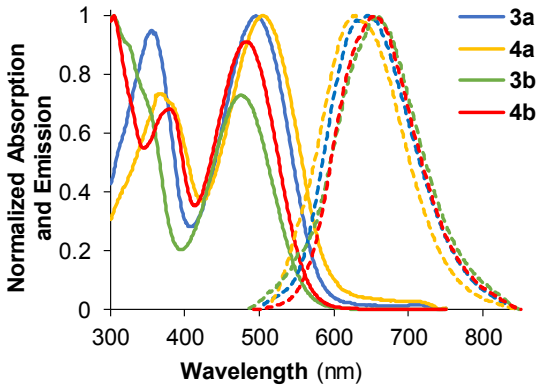


Fig. 1. Normalized absorption (full line) and emission (dashed line) spectra for compounds **3a-b** and **4a-b**, in ethanol at 21 ± 2 °C.

Table 2
Electrochemical data for synthesized dyes **4a-b** and reference dye **N719**.

Cpds	Reduction Potential[a] (V)	Oxidation Potential[a] (V)	E_{HOMO}[b] (eV)	E_{LUMO}[b] (eV)	Band gap[c] (eV)
4a	−1.80	0.35	−4.74	−2.59	2.15
4b	−1.78	0.72	−5.11	−2.61	2.50
N719	−2.04	0.46	−4.85	−2.35	2.50

[a] Measurements were performed in dry DMF containing 1.0 mM in each compounds and 1.0 mM $[NBu_4][BF_4]$ as base electrolyte at a carbon working electrode at scan rate of 0.01 V s^{-1}. All E values are quoted *vs.* the ferrocenium/ferrocene-couple. E_{pc} and E_{pa} correspond to the potentials of cathodic and anodic peaks, respectively.

[b] E_{HOMO} = -(4.39 + Eox) (eV) and E_{LUMO} = -(Ered + 4.39) (eV).

[c] Calculated from the difference between the onset potentials of oxidation and reduction.

2.4. Evaluation of dyes *4a-b* as sensitizers for TiO_2 in dye-sensitized solar cells

The photocurrent-voltage responses of the DSSCs produced using the synthesized dyes **4a-b**, reference dye **N719**, and co-adsorption of **N719** followed by dye **4a** or **4b**, are presented in Fig. 2a, showing typical photodiodes shapes for all curves. The electrical parameters of the DSSCs (Short-circuit Current Density - J_{SC}, Open Circuit Voltage - V_{OC}, Maximum Power Point - *MPP*, Fill Factor - *FF*, and efficiency - η) are summarized in Table 3.

DSSCs sensitized with dye **4b** shows an efficiency of 4.51 %. The best conversion efficiency of this cell (about 55 % of the photovoltaic performance of the reference cell sensitized with dye **N719**), results from the improved electron injection and less dark current, as indicated by the higher J_{SC} (9.36 mA cm^{-2}) and V_{OC} (0.63 V). Dye **4b** presents the highest band gap of the synthesized dyes (2.50 V), that is very similar to that of the reference dye **N719**. These results show that dye **4b** bearing a *N*,*N*-diphenylanilino donor moiety conjugated with a cyanoacetic acid acceptor/anchoring group, through a thienyl-benzothiadiazole spacer has good potential as sensitizer for TiO_2. The evaluation of this dye as TiO_2 sensitizer in DSSC, in different conditions has been

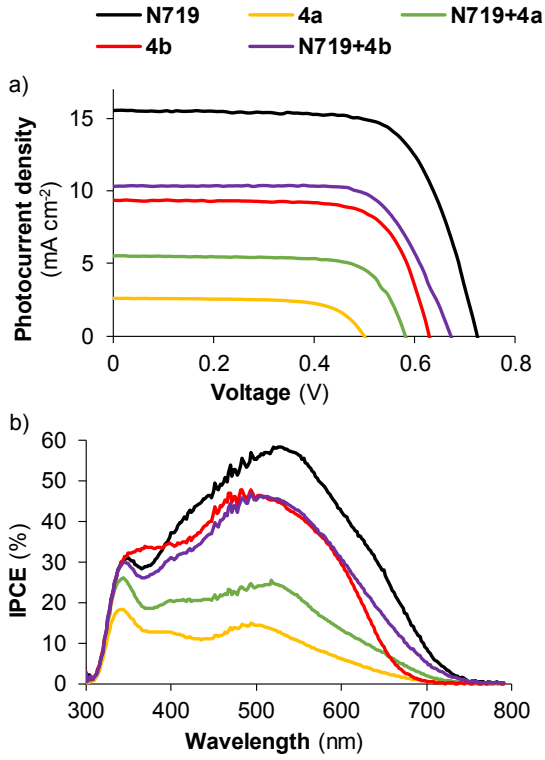


Fig. 2. a) Photocurrent – voltage curves of the DSSCs prepared with synthesized dyes **4a-b**, reference **N719**, and co-adsorption of **N719** followed by dyes **4**. b) IPCE spectra of the DSSCs based on the synthesized dyes **4a-b**, reference dye **N719**, and co-adsorption of **N719** followed by dyes **4a-b**.

Table 3
Electrical metrics of DSSCs with dyes **4a-b**, reference dye **N719**, and co-adsorption of **N719** followed by dyes **4a-b**.

Sensitizer	V_{OC} (V)	J_{SC} (mA cm^{-2})	*MPP*	*FF*	η (%)
4a	0.50	2.60	0.90	0.69	0.95
4b	0.63	9.36	4.26	0.72	4.51
N719	0.72	15.55	7.86	0.70	8.19
N719 + 4a	0.58	5.51	2.36	0.74	2.49
N719 + 4b	0.67	10.30	4.93	0.71	5.22

previously reported, with photovoltaic cell efficiencies of 3.77 % [17a], 5.0 % [17b], 5.01 % [17c], and 4.76–6.49 % [17d].

The DSSC prepared using dye **4a** exhibited low photovoltaic performance with an efficiency of 0.95 %, due to the inefficient electron injection into TiO_2 conduction band indicated by the lower J_{SC} (2.60 mA cm^{-2}), and slightly less *FF* (0.69). This result was assigned to the low oxidation potential of the dye, that decreases the ability of the electrolyte to regenerate the dye to its initial state. Fig. 2b presenting the IPCE spectra, supports this assumption showing low incident photon to electron efficiency over the UV–vis spectral region.

Fig. 2b also shows a peak at λ ~350 nm that is the response from TiO_2 itself. It is interesting to note that adsorption of all dyes **4** on TiO_2 leads to a decrease of photocurrent yield from TiO_2. The reason for this is the intrinsic absorption of light by the dyes, that does not lead to injection of the photoelectrons into TiO_2.

For the future work, an interesting option would be the evaluation of the sensitizers **4a-b** using an electrolyte solution with a lower redox potential that could possibly regenerate dye **4a**.

DSSCs with ruthenium based dyes yield maximum efficiencies using thicker TiO_2 mesoporous films due to their low molar extinction coefficients. In contrast, organic dyes commonly have higher molar extinction coefficients, which allows using thinner TiO_2 films and reduction of losses for charge transport, but display narrow absorption bands decreasing the light harvesting. To combine the different advantages of both metal-free dyes and Ru-dyes, a step-wise co-adsorption study was performed by first adsorbing of **N719** followed by dyes **4** (Table 3, Fig. 2). Co-adsorption with different dyes covering broader spectral region might be an effective and economic way to increase the efficiency of the solar cells but also might be very useful in the aggregates suppression usually observed on these systems.

It was observed that the photovoltaic performance of the cells was improved by co-sensitization approach. Therefore, the addition of the synthesized dye **4a** or **4b** to the first adsorbed **N719** results in higher short circuit current and open circuit voltage, giving photovoltaic efficiencies of 2.49 % for the cell sensitized with **N719** + **4a**, and 5.22 % for the cell sensitized with **N719** + **4b**. These results represents an improvement of cell efficiencies of 260 % for sensitizer **4a** or 11 % for the sensitizer **4b** bearing a *N*,*N*-diphenylanilino donor moiety.

3. Experimental

3.1. Materials and methods

2-Cyanoacetic acid, 4-(diphenylamino)phenylboronic acid pinacol ester, 5′-hexyl-2,2′-bithiophene-5-boronic acid pinacol ester, and 4,7-dibromobenzo[*c*]-1,2,5-thiadiazole were purchased from Aldrich. 5-Formyl-2-thiopheneboronic acid was purchased from Acros Organics. All commercially available reagents and solvents were used as received. Reaction progress was monitored by thin layer chromatography, using 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel 60 F254), and spots were visualized under UV light. Purification was achieved by silica gel column chromatography (Merck Kieselgel, 230–400 mesh). NMR spectra were obtained on a Bruker Avance II 400 at an operating frequency of 400 MHz for ^1H, using the solvent peak as internal reference. The solvent is indicated in parenthesis before the chemical shift values (δ relative to TMS). Peak assignments were made by comparison of chemical shifts, peak multiplicities and *J* values. UV–vis absorption spectra were obtained using a Shimadzu UV/2501 PC spectrophotometer. Fluorescence spectra were collected using a FluoroMax-4 spectrofluorometer. The relative fluorescence quantum yields were determined using fluorescein in a 0.1 M aqueous solution of NaOH (ϕ_F = 0.79) as reference [19]. Mass spectrometry analysis were performed at the C.A.C.T.I. – Unidad de Espectrometria de Masas of the University of Vigo, Spain.

3.2. General procedure for the synthesis of benzothiadiazole derivatives **2** and **3a-b** through Suzuki-Miyaura cross-coupling

Precursors **1–2** (0.5 mmol) were coupled with heterocyclic boronic acids (0.6 mmol) in a mixture of DME (8 mL), ethanol (2 mL), aqueous 2 M Na_2CO_3 (1 mL) and $Pd(PPh_3)_4$ (5 mol %) at 80 °C, under nitrogen. The reaction was monitored by TLC, which determined the reaction time (48 h). After cooling, the mixture was extracted with chloroform (3 × 20 mL) and a saturated solution of NaCl were added (20 mL) and the phases were separated. The organic phase was washed with water (3 × 10 mL) and with 10 mL of a solution of NaOH (10 %). The organic phase obtained was dried ($MgSO_4$), filtered, and the solvent removed to give a crude mixture. The crude product was purified through a silica gel chromatography column using mixtures of chloroform and light petroleum of increasing polarity to afford the coupled products **2**. Recrystallization from *n*-hexane/dichloromethane gave the pure compounds.

3.2.1. 5-(7′-Bromobenzo[c][1,2,5]thiadiazol-4′-yl)thiophene-2-carbaldehyde (**2**). [CAS: 1309922-61-9]

Yellow solid (40 %). λ_{max}(ethanol)/nm 394 ε/dm^3 mol^{-1} cm^{-1} 11,397.^1H NMR (DMSO-d_6, 400 MHz) δ 8.12 (d, 1H, *J* = 4.0 Hz, 3-*H*), 8.13 (d, 1H, *J* = 7.6 Hz, 5′-*H*), 8.20 (d, 1H, *J* = 7.6 Hz, 6′-*H*), 8.26 (d, 1H, *J* = 4.0 Hz, 4-*H*), 10.0 (s, 1H, C*H*O) ppm.

3.2.2. 5-(7′-(5‴-Hexyl-(2″,2‴-bithiophen)-5″-yl)benzo[c][1,2,5]thiadiazol-4′-yl)thiophene-2-carbaldehyde (**3a**)

Black solid (56 %). Mp. 131–133 °C. IR (liquid film): ν 1647 (C=O) cm^{-1}. λ_{max} (ethanol)/nm 495 ε/$M^{-1}cm^{-1}$ 31,640.^1H NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, 3H, CH_3), 1.32–1.36 (m, 6H, $CH_3(CH_2)_3$), 1.69–1.72 (m, 2H, CH_2CH$_2$-thiophen), 2.81 (t, 2H, CH_2-thiophen), 6.73 (d, 1H, *J* = 4.3 Hz, 4‴-*H*), 7.12 (d, 1H, *J* = 3.6 Hz, 3‴-*H*), 7.18 (d, 1H, *J* = 4.0 Hz, 3″-*H*), 7.82–7.85 (m, 2H, 6′- and 4″-*H*), 7.95 (d, 1H, *J* = 7.6 Hz, 5′-*H*), 8.07 (d, 1H, *J* = 4.0 Hz, 3-*H*), 8.18 (d, 1H, *J* = 4.4 Hz, 4-*H*), 9.97 (s, 1H, C*H*O) ppm. MS (ESI) *m/z* (%) = 495 ([M + H]$^+$, 100), 466 (23), 391 (18), 247 (17). HRMS: *m/z* (ESI) [M + H]$^+$ found 495.06877; $C_{25}H_{23}N_2OS_4$ requires 495.06932.

3.2.3. 5-(7′-(4″-Diphenylamino)phenyl)benzo[c][1,2,5]thiadiazol-4′-yl) thiophene-2-carbaldehyde (**3b**) [17]

Orange solid (61 %). IR (liquid film): ν 1650 (C=O) cm^{-1}. λ_{max} (ethanol)/nm 475 ε/$M^{-1}cm^{-1}$ 26,393.^1H NMR ($CDCl_3$, 400 MHz) δ 7.11 (t, 2H, 2 × 4‴-*H*), 7.19–7.32 (m, 10H, 2 × 2‴-*H*, 2 × 3‴-*H*, 2 × 5‴-*H*, 2 × 6‴-*H*, 3″-*H* and 5″-*H*), 7.74 (d, 1H, *J* = 7.6 Hz, 6′-*H*), 7.86 (d, 1H, *J* = 4.0 Hz, 3-*H*), 7.89 (d, 2H, *J* = 8.8 Hz, 2″- and 6″-*H*), 8.05 (d, 1H, *J* = 7.6 Hz, 5′-*H*), 8.22 (d, 1H, *J* = 4.0 Hz, 4-*H*), 9.99 (s, 1H, C*H*O) ppm.

3.3. General procedure for the synthesis of cyanoacetic derivatives **4a-b** by Knoevenagel condensation

To a solution of the appropriate aldehyde **3a-b** (2.5 mmol) and cyanoacetic acid (3 mmol) in acetonitrile (15 mL) was added 4 drops of piperidine. The mixture was refluxed for 8 h then cooled down to room temperature. The organic solvent was partially evaporated and ethyl ether was added to induce precipitation. The precipitate was filtered and washed with ethyl ether to give the pure dyes **3a-b**.

3.3.1. 2-Cyano-3-(5′-(7″-(5‴′-hexyl-(2‴,2‴′-bithiophen)-5‴-yl)benzo[c][1,2,5]thiadiazol-4″-yl)thiophen-2′-yl)acetic acid (**4a**)

Black solid (43 %). Mp. > 250 °C. IR (liquid film): ν 3355 (O-H), 2211 (C≡N), 1612 (C=O) cm^{-1}. λ_{max} (ethanol)/nm 506 ε/$M^{-1}cm^{-1}$ 28,556.^1H NMR (DMSO-d_6, 400 MHz) δ 0.86 (t, 3H, CH_3), 1.28–1.30 (m, 6H, $CH_3(CH_2)_3$), 1.52–1.57 (m, 2H, CH_2CH$_2$-thiophen), 2.87 (t, 2H, CH_2-thiophen), 6.85 (d, 1H, *J* = 3.6 Hz, 4‴′-*H*), 7.62 (d, 1H, *J* = 3.6 Hz, 3‴′-*H*), 7.37 (d, 1H, *J* = 4.0 Hz, 3‴-*H*), 7.80 (d, 1H,

J = 4.0 Hz, 4‴-*H*), 8.11–8.22 (m, 5H, 6″-*H*, 5″-*H*, 4′-*H*, 3′-*H*, 3-*H*) ppm. MS (ESI) *m/z* (%) = 561 ($[M]^+$, 30), 533 (100), 494 (33), 466 (41), 381 (50), 359 (45), 353 (47), 341 (51), 313 (44). HRMS: *m/z* (ESI) $[M]^+$ found 561.06676; $C_{28}H_{23}N_3O_2S_4$ requires 561.06731.

3.3.2. 2-Cyano-3-(5′-(7″-(4‴-diphenylamino)phenyl)benzo[c][1,2,5] thiadiazol-4″-yl)thiophen-2′-yl)acetic acid (**4b**) [17]

Orange solid (51 %). IR (liquid film): ν 3355 (O-H), 2210 (C≡N), 1592 (C=O) cm^{-1}. λ_{max} (ethanol)/nm 482 $\varepsilon/M^{-1}cm^{-1}$ 23,769.^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.08–7.12 (m, 8H, 3‴-*H*, 5‴-*H*, 2 × 2‴-*H*, 2 × 4‴-*H* and 2 × 6‴-*H*), 7.33–7.37 (m, 4H, 2 × 3‴-*H* and 2 × 5‴-*H*), 7.80 (d, 1H, *J* = 4.0 Hz, 3′-*H*), 7.90 (d, 1H, *J* = 7.6 Hz, 6″-*H*), 7.97 (d, 2H, *J* = 8.8 Hz, 2‴-*H* and 6‴-*H*), 8.10 (s, 1H, 3-*H*) 8.20–8.24 (m, 2H, 5″-*H* and 4′-*H*) ppm.

3.4. Cyclic voltammetry

The measurements were performed using AUTOLAB PGSTAT302 N electrochemical station in a three electrode two compartment cell using vitreous carbon as working electrode, platinum wire as counter-electrode and Ag/AgCl electrode as reference. The dye concentration was 1 mM with 1 mM of $[NBu_4][BF_4]$ as supporting electrolyte in dry *N*,*N*-dymethylformamide. Before the electrochemical measurements, solutions were deaerated by bubbling of nitrogen for 15 min. Cyclic voltammograms were recorded at potential sweep-rates of 20, 50, 100 and 200 mV s^{-1}. Fc^+/Fc couple was used as internal redox reference [20,21].

3.5. Dye-sensitized solar cell preparation and measurements of their photovoltaic performance

Typically, a dye-sensitized solar cell consists of: i) a mesoporous layer of TiO_2 where the dye molecules are adsorbed, both comprising the working electrode; ii) platinum counter-electrode; and iii) electrolyte with the iodide/triiodide redox couple. The working electrodes were applied on FTO-coated glasses (TCO22-7, 2.2 mm thickness, 7 Ω/square, Solaronix, Switzerland) by screen-printing and sintering at 500 °C for 1 h (0.5 × 0.5 cm^2 active area, and 12 μm of thickness) a layer of TiO_2 paste (TiO_2 paste DSL 18NR-AO T/SP). TiO_2 electrodes were then immersed into a 0.5 mM dye solution in absolute ethanol and kept at 23 ± 2 °C for 48 h. For co-adsorption studies the TiO_2 electrodes were immersed into a 0.5 mM solution of **N719** in absolute ethanol for 48 h, rinsed with absolute ethanol, and immersed into a 0.5 mM dye **4** solution for another 48 h.

Two holes were drilled in the FTO-coated glass of the counter-electrode, before applying the layer of Pt-catalyst (Platisol T/SP, Solaronix, Switzerland). The layer of platinum was screen-printed on the FTO side of the glasses and sintered at 450 °C for 20 min.

The dye-covered TiO_2 electrode and the Pt counter-electrode were assembled into a sandwich type cell and sealed with a hot-melt foil of 25 μm (Surlyn, Meltonix 1170–25, Solaronix, Switzerland) by hot-pressing. The electrolyte (Iodolyte AN-50, Solaronix, Switzerland) was injected into the cell, and the injection holes were then sealed by Surlyn®, and covered with lamella glass using a soldering iron for melting the polymer sealant.

A solar simulator (Newport, USA) was used to give an irradiance of 100 mW cm^{-2} (AM 1.5G) at the surface of the solar cells. The simulator was calibrated using a calibrated Si cell. The current-voltage characteristics of the cells under 1-sun illumination were obtained applying an external potential bias to the cell and measuring the generated photocurrent with ZENNIUM workstation (Ref. 2425-C, Zahner Elektrik, Germany). Photovoltaic performance was measured using a metal mask with an aperture area of 0.25 cm^2.

The IPCE spectra were acquired using a PC-operated setup consisting of a 300 W Xenon lamp as a light source (Newport 66,902), a monochromator (Newport Cornerstone 74,125), a Lock-in amplifier (Newport Merlin 70,104), set of optical filters, and a light chopper. The photon flux of light incident on the samples was normalized using a calibrated silicon detector (Newport 70,356). The bias light was supplied by a 100 W halogen lamp, and the light intensity was adjusted to 0.3 Sun by the driven current from a constant current source. Measurements were made at 2 nm wavelength intervals between 290 and 800 nm.

4. Conclusions

Starting from commercially available precursors, and using straightforward and easy synthetic/purification methodologies, benzothiadiazole-based push-pull heterocyclic chromophores **3–4** were obtained in good yields.

Studies concerning the optical and redox properties, and photovoltaic behavior of the DSSCs produced using the synthesized dyes were performed in order to study the effect the different donor groups (aromatic or heterocyclic). These studies demonstrated that the 5′-hexyl-2,2′-bithienyl (**4a**) donating moiety is more easily oxidized when compared to *N*,*N*-diphenylanilino (**4b**) group. However, the low oxidation potential greatly increases the chance for back electron transfer to the electrolyte and decreases the ability of the electrolyte to regenerate the dye to its initial state.

DSSC sensitized with dye **4b**, bearing a *N*,*N*-diphenylanilino electron donating moiety, exhibits the best conversion efficiency of the synthesized dyes 4.51 %, mainly due to enhanced short circuit current. Co-adsorption studies were performed by the step-wise methodology by first adsorbing of **N719** on TiO_2 followed by dye **4a** or **4b**. The achieved enhanced cell efficiencies were of 2.49 % for sensitizer **N719** + **4a**, and 5.22 % for sensitizer **N719** + **4b**, which represents an improvement of cell efficiencies of 260 % for sensitizer **4a** or 11 % for the sensitizer **4b**, mainly due to the enhancement of electron injection and suppressing the dark current.

Further tuning of the molecular structure of all chromophores is likely to produce even more enhanced efficiencies. Additionally, adjusting electrolyte composition to improve the efficiency of the dyes as sensitizers is the subject of a separate study.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.10.038.

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